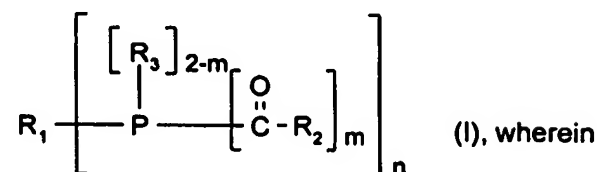


Claims

## 1. A process for the preparation of acylphosphanes of formula I




**n** and **m** are each independently of the other 1 or 2;


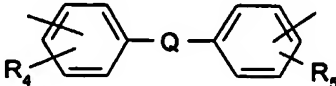
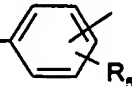
**R<sub>1</sub>**, if **n = 1**, is

C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>2</sub>-C<sub>18</sub>alkyl which is interrupted by one or several non-successive O atoms; phenyl-C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>2</sub>-C<sub>8</sub>alkenyl, phenyl, naphthyl, biphenyl, C<sub>5</sub>-C<sub>12</sub>cycloalkyl or a 5- or 6-membered O-, S- or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl, C<sub>5</sub>-C<sub>12</sub>cycloalkyl or the 5- or 6-membered O-, S- or N-containing heterocyclic ring being unsubstituted or substituted by one to five halogen, C<sub>1</sub>-C<sub>8</sub>alkyl, C<sub>1</sub>-C<sub>8</sub>alkylthio, C<sub>1</sub>-C<sub>8</sub>alkoxy and/or -N(R<sub>8</sub>)<sub>2</sub>;

**R<sub>1</sub>**, if **n = 2**, is

C<sub>1</sub>-C<sub>18</sub>alkylene, C<sub>2</sub>-C<sub>18</sub>alkylene which is interrupted by one or several non-successive O atoms; or R<sub>1</sub> is C<sub>1</sub>-C<sub>8</sub>alkylene which is substituted by C<sub>1</sub>-C<sub>4</sub>alkoxy, phenyl, C<sub>1</sub>-C<sub>4</sub>alkyl-phenyl, phenyl-C<sub>1</sub>-C<sub>4</sub>alkyl or C<sub>1</sub>-C<sub>8</sub>alkoxyphenyl; or R<sub>1</sub> is phenylene or xylylene, which radicals are unsubstituted or substituted by one to three C<sub>1</sub>-C<sub>4</sub>alkyl and/or C<sub>1</sub>-C<sub>4</sub>alkoxy, or

R<sub>1</sub> is a -CH<sub>2</sub>CH=CHCH<sub>2</sub>-, -CH<sub>2</sub>-C≡C-CH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>--CH<sub>2</sub>CH<sub>2</sub>-,

-CH<sub>2</sub>CH<sub>2</sub>O--OCH<sub>2</sub>CH<sub>2</sub>- or -Q- group;

**R<sub>2</sub>** is C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>3</sub>-C<sub>12</sub>cycloalkyl, C<sub>2</sub>-C<sub>18</sub>alkenyl, phenyl-C<sub>1</sub>-C<sub>4</sub>alkyl, phenyl, naphthyl, biphenyl or a 5- or 6-membered O-, S- or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl or the 5- or 6-membered O-, S- or N-containing heterocyclic ring being unsubstituted or substituted by one to five halogen, C<sub>1</sub>-C<sub>8</sub>alkyl, C<sub>1</sub>-C<sub>8</sub>alkoxy and/or C<sub>1</sub>-C<sub>8</sub>alkylthio;

**R<sub>3</sub>** is C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>2</sub>-C<sub>18</sub>alkyl which is interrupted by one or several non-successive O atoms or which is interrupted by -CO-, -COO-, -OCO-, -OCOO-, -CO-N(R<sub>9</sub>)-, -N(R<sub>9</sub>)-CO-,

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$-N(R_9)-CO-N(R_9)-$ ,  $-N(R_9)-COO-$ ;  $C_1-C_{18}$  alkyl substituted by  $-OR_{10}$ ,  $-OCO-R_{10}$ ,  $-COO-R_{10}$ ,  $-N(R_9)-CO-R_{10}$ ,  $-CO-N(R_9)-R_{10}$ ,  $-C(R_{11})=C(R_{12})-CO-OR_{10}$  or  $-C(R_{11})=C(R_{12})$ -phenyl;

$C_2-C_{12}$ alkenyl or  $C_2-C_{12}$ alkenyl which is interrupted by one or several non-successive O atoms; phenyl- $C_1-C_4$ alkyl, phenyl, naphthyl, biphenyl,  $C_5-C_{12}$ cycloalkyl or a 5- or 6-membered O-, S- or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl,  $C_5-C_{12}$ cycloalkyl or the 5- or 6-membered O-, S- or N-containing heterocyclic ring being unsubstituted or substituted by one to five halogen,  $C_1-C_8$ alkyl,  $C_1-C_8$ alkylthio  $C_1-C_8$ alkoxy and/or  $-N(R_8)_2$ ; or  $R_3$  is  $-CO-OR_9$  or  $-CO-N(R_9)_2$ ;

$Q$  is a single bond,  $CR_6R_7$ ,  $-O-$  or  $-S-$ ;

$R_4$  and  $R_5$  are each independently of the other hydrogen,  $C_1-C_4$ alkyl or  $C_1-C_4$ alkoxy;

$R_6$  and  $R_7$  are each independently of the other hydrogen or  $C_1-C_4$ alkyl;

$R_8$  is  $C_1-C_{18}$  alkyl,  $C_2-C_{18}$  alkyl which is interrupted by one or several non-successive O-atoms; or  $-N(R_8)_2$  forms a 5- or 6-membered O-, S- or N-containing heterocyclic ring;

$R_9$  is hydrogen,  $C_1-C_{18}$ alkyl,  $C_2-C_{18}$ alkyl which is interrupted by one or several non-successive O atoms,  $C_3-C_{12}$ -cycloalkyl,  $C_2-C_{18}$ -alkenyl, phenyl- $C_1-C_4$ -alkyl, phenyl, naphthyl, pyridyl, the radicals phenyl, naphthyl or pyridyl being unsubstituted or substituted by one to five  $C_1-C_8$ -alkyl,  $C_1-C_8$ -alkoxy,  $C_1-C_8$ -alkylthio and/or halogen; or  $-N(R_9)_2$  forms a 5- or 6-membered O-, S- or N-containing heterocyclic ring;

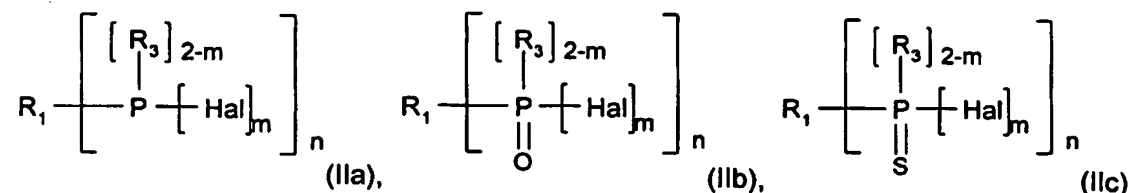
$R_{10}$  is  $C_1-C_{18}$ alkyl,  $C_2-C_{18}$ alkyl which is interrupted by one or several non-successive O-atoms,  $C_3-C_{12}$ -cycloalkyl, phenyl- $C_1-C_4$ -alkyl,  $C_2-C_{18}$ -alkenyl, phenyl, naphthyl, biphenyl; the radicals phenyl- $C_1-C_4$ -alkyl, phenyl, naphthyl or biphenyl being unsubstituted or substituted by one to five  $C_1-C_8$ -alkyl,  $C_1-C_8$ -alkoxy,  $C_1-C_8$ -alkylthio and/or halogen;

$R_{11}$  is hydrogen or  $C_1-C_4$ -alkyl;

$R_{12}$  is hydrogen or  $C_1-C_4$ -alkyl;

by

- (1) reacting a phosphorous halide of formula IIa or a phosphorous halide oxide of formula IIb or a phosphorous halide sulfide of formula IIc

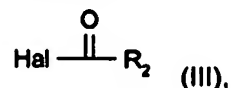


wherein  $R_1$ ,  $R_3$ ,  $n$  and  $m$  have the meaning cited above and Hal is F, Cl, Br or I;

with an alkali metal in a solvent (metallation) in the presence of a proton source (reduction);

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(2) subsequent reaction with m acid halides of formula III



wherein R<sub>2</sub>, Hal and m have the meaning cited above.

2. A process according to claim 1, wherein in step (1) the metallation is carried out by reacting a compound of the formula IIa, IIb, or IIc with an alkali metal in a solvent, whereby a metallized phosphanide of the formula V



is formed together with cyclic phosphanes (R<sub>1</sub>P)<sub>n</sub>, n ≥ 3 as intermediates, wherein Me is lithium, sodium or potassium or magnesium in combination with lithium, and R<sub>1</sub> is as defined in claim 1; and

wherein the reduction is carried out by reacting the intermediate V and/or (R<sub>1</sub>P)<sub>n</sub>, n ≥ 3 with a proton source.

3. A process according to claim 2, wherein

the alkali metal is sodium;

the proton source is selected from sterically hindered alcohols, trialkylamine hydrohalogenes, bisarylamines, malono nitrile, malonic acid esters, amidine hydrohalogene and carboxylic acids;

the solvent is benzene, toluene, o-, m- or p-xylene, mesitylene, ethylbenzene, diphenylethane, 1,2,3,4-tetrahydronaphthalene (tetraline), isopropylbenzene (cumol) and mixtures thereof; and

the reaction temperature of step (1) is in the range from -20°C to +160°C.

4. A process according to claim 3, wherein the sterically hindered alcohol is selected from the group consisting of secondary or tertiary C<sub>3</sub>-C<sub>18</sub>alcohols, preferably of t-butanol, tert.-amyl-alcohol, 3-methyl-3-pentanol, 3-ethyl-3-pentanol, triphenylmethanol, 3,7-dimethyl-3-octanol, 2-methyl-1-phenyl-2-propanol, 2-methyl-4-phenyl-2-butanol, fenchyl alcohol, 2,4-dimethyl-3-pentanol, 1-dimethylamino-2-propanol or hexylene glycol.

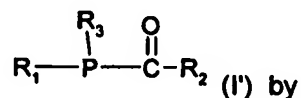
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5. A process according to any one of claims 1-3, wherein the metallation is carried out in the presence of catalytic amounts of alkali or earth alkali hydroxides or of Na, K or Li alcoholates or of alcohols, preferably sterically hindered alcoholates or alcohols.

6. A process according to any one of claims 1-3, wherein the metallation and reduction step is carried out in the presence of an activator.

7. A process according to claim 6, wherein the activator is an amine selected from triethylamine, tributylamine, piperidine, morpholine, N-methylpiperidine, N-methyl morpholine or a polyamine such as N,N,N',N'-tetramethylethylenediamine (TMEDA).

8. A process according to claim 1 for the preparation of monoacylphosphanes of the formula I'

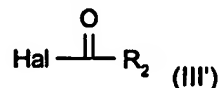


(1) reacting organic phosphorus halides of formula II'



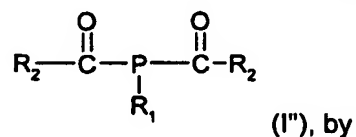
with an alkali metal in a solvent in the presence of a proton source;

(2) subsequent reaction with an acid halide of formula III'



followed by the reaction with an electrophilic compound  $\text{R}_3\text{-Hal}$  or vice versa, wherein  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  and Hal are as defined in claim 1.

9. A process according to claim 1 for the preparation of symmetric bisacylphosphanes of the formula I'' (compounds of the formula I with  $n=1$  and  $m=2$ )



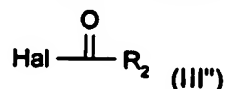
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- (1) reacting organic phosphorus halides of formula II''



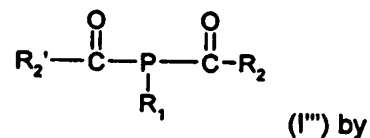
with an alkali metal in a solvent in the presence of a proton source;

- (2) subsequent reaction with an acid halide of formula III''



wherein  $R_1$  and  $R_2$  and Hal are as defined in claim 1.

10. A process according to claim 1 for the preparation of **unsymmetric bisacylphosphanes** of the formula I'''

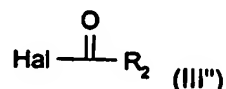


- (1) reacting organic phosphorus halides of formula II''

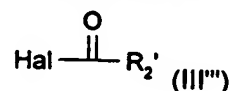


with an alkali metal in a solvent in the presence of a proton source;

- (2) subsequent reaction with an acid halide of formula III''



- (3) subsequent reaction with a second acid halide III'''



wherein

$R_1$  is as defined in claim 1 and

$R_2$  and  $R_2'$  independently of one another are as defined in claim 1 under  $R_2$  with the proviso that  $R_2$  is not equal  $R_2'$ ,

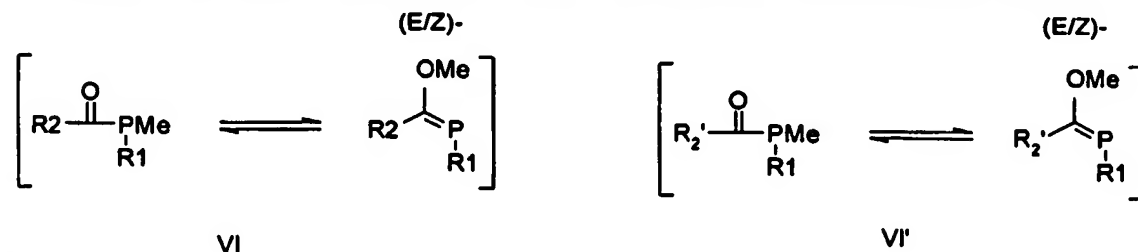
Hal is as defined in claim 1.

11. A process according to claim 1, wherein step (1) is carried out by reacting diphosphanes of the formula  $(R_1)_2-P-P(R_1)_2$  or polyphosphanes of the formula  $[R_1P]_n$ , wherein  $R_1$  is as defined above and  $n$  is  $\geq 3$ , with an alkali metal in a solvent in the presence of a proton

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source; followed by the reaction with acid halides (III, III', III'', III''') and/or by reaction with electrophilic compounds R<sub>3</sub>-Hal.

12. A process for the preparation of mono acylated phosphanes of the formula VI and VI'



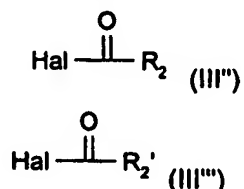
by

(1) reacting organic phosphorus halides of formula II''



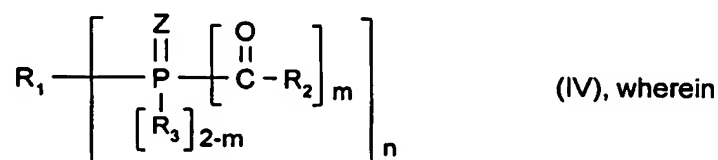
with an alkali metal in a solvent in the presence of a proton source;

(2) subsequent reaction with an acid halide of formula III'' or III'''



wherein R<sub>1</sub>, R<sub>2</sub> are as defined in claim 1 R<sub>2</sub>' is as defined in claim 10 and Me is Li, Na, K or Mg in combination with Li.

13. A process for the preparation of acylphosphane oxides and acylphosphane sulfides of formula IV



R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, n and m are as defined in claim 1, and Z is O or S,

by oxidation or reaction with sulfur of the acylphosphane of formula I, I', I'' or I'''

as defined in claims 1, 8, 9 and 10.